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A New Ultra-thin Film of Solid Polymer Electrolyte Prepared by Plasma Polymerization[1)]

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An ultra-thin polymer film containing sulfonic ester group is prepared by polymerization of methyl benzenesulfonate and octamethylcyclotetrasiloxane in glow discharge. The sulfonic ester group is transformed to lithium sulfonate group by the treatment with LiI. Hybridization of plasma polymer containing lithium sulfonate group with poly(ethylene oxide) forms only lithium ion conductive films.

Extensive studies have recently been done on solid polymer electrolytes prepared by treatment of polyethers such as poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) with alkali metal salt.[2-4)] We have prepared ultra-thin solid polymer electrolyte by hybridization of plasma polymerized octamethylcyclotetrasiloxane (OMCTS) with PPO and $LiClO_4$.[5)] In above described solid polymer electrolytes, both anion and cation are mobile. When this kind of solid polymer electrolyte is used in electrochemical devices, charge separation by unbalanced distribution of anion and cation takes place, which results in the remarkable increase of electric resistance.[6)] Recently, in order to overcome this problem, a few works on the solid polymer electrolyte with only one mobile species appear.[6-8)] Along this line, we have focused on the preparation of a ultra-thin film of polymer electrolyte with sulfonic acid group. This paper describes the preparation of the ultra-thin film containing lithium sulfonate by plasma polymerization of OMCTS and methyl benzenesulfonate, followed by the transformation of the resulting sulfonic ester into lithium sulfonate.

Methyl benzenesulfonate was selected as one component of plasma polymer; introduced sulfonic ester can be transformed into lithium sulfonate by the treatment of LiI. Plasma polymerization was performed in the glass chamber (9 cm diameter and 35 cm height) equipped with capacitively coupled inner electrodes connected with an RF power supply (13.56 MHz). Glass substrates deposited with gold were placed between the electrodes. Gases, i.e. Ar [10 cm^3(STP)/min], OMCTS [2 cm^3(STP)/min] and methyl benzenesulfonate [various flow rate], were introduced into the glass chamber. The pressure inside the chamber was maintained at 0.05 Torr by controlling a valve connecting to vacuum pump. Under these conditions, RF power at 20 W was turned on. The resulting plasma polymer layers deposited on substrates were about 1 μm thick.

These polymers were soaked in sat. LiI/propylene carbonate (PC) solution at

50 °C. The treated plasma polymer layer was washed with PC to remove LiI and alkyl iodide, and then dried at 50 °C under reduced pressure (10^{-3} Torr).

The plasma polymer having lithium sulfonate was hybridized with PEO by soaking in butanol (45%)-PEO [$\overline{MW}$, 300] (55%) solution for 1 h, and then dried under vacuum to evaporate butanol. The preparation of an ultra-thin (≈1 μm) film of hybrid polymer electrolyte was thus completed. The content of lithium ion in the film was determined by an atomic absorption spectrophotometric measurement. The content of PEO in the film was determined by weighing the film before and after hybridization. The ionic conductivity of the hybrid polymer electrolyte (plasma polymer with lithium sulfonate - PEO) was estimated by an AC impedance measurement over the frequency range of 2×10^{2}-2×10^{4} Hz with a vector impedance meter. Two arcs were distinguished in complex impedance plot. The first arc, for high frequency range, is attributed to the bulk electrolyte impedance.[7)] Thus the arc was extrapolated to the real axis to obtain the bulk electrolyte resistance.

ESCA S_{2p} spectrum of the plasma polymer before LiI treatment was shown in Fig.1. The peak at 169.3 eV was assigned to sulfonic ester group. The peak at 164.5 eV was attributed to sulfoxide group.[9,10)] This result suggests that the plasma polymer from methyl benzenesulfonate contains sulfonic ester group.

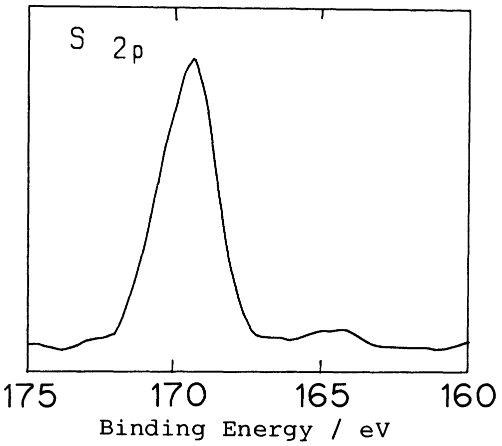

Fig. 1. ESCA S_{2p} spectrum of plasma polymer before LiI treatment.

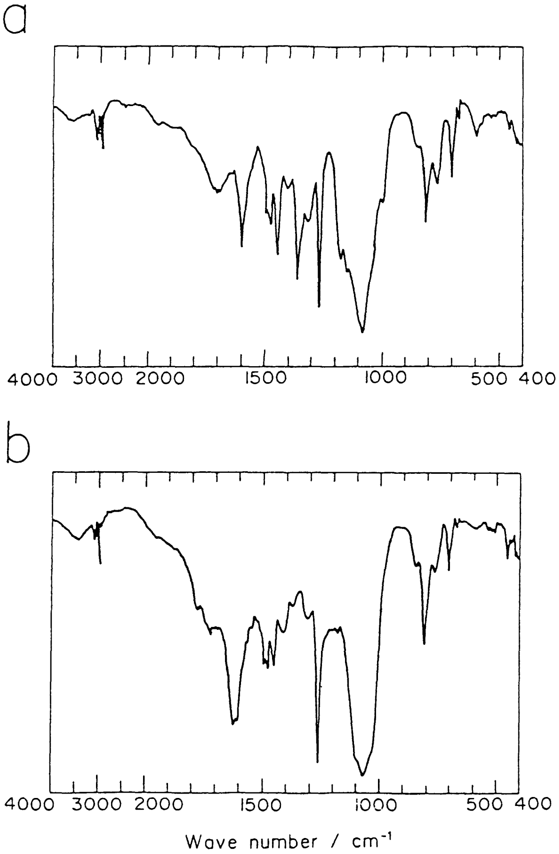

Fig. 2. IR spectra of plasma polymers formed from OMCTS [2 cm^3 (STP)/min] and methyl benzenesulfonate [1.2 cm^3/min] before (a) and after (b) LiI treatment.

Figure 2 illustrates IR spectra of the plasma polymer from OMCTS and methyl benzenesulfonate before [Fig.2(a)] and after [Fig.2(b)] LiI treatment. The two absorption peaks at 1360cm^{-1} and 1180cm^{-1} in Fig.2(a) were attributed to the sulfonic ester group.[11)] The absorptions at 2960, 2900, 1410, 1260, 1200-1000, 840, 800 cm^{-1} were common with those of poly(dimethylsiloxane). The other peaks at 3050, 1600, 1490, 1480, 1450 cm^{-1} were attributable to benzene ring. In Fig.2(b), the two characteristic peaks of sulfonic ester group completely disappeared. The result indicates that the reaction of sulfonic ester with LiI gave lithium sulfonate. The peaks of lithium sulfonate at 1175 cm^{-1} and 1055 cm^{-1} 11) are overlapped with the strong absorption of Si-O-Si and Si-O-C (1180-1000 cm^{-1}). From EPMA observation, the Si/S atom ratio was kept unchanged before and after the LiI treatment, and iodine could not be detected. These results suggest that lithium sulfonate groups were fixed on polymer backbone.

The plasma polymer after the LiI treatment was soaked in 0.5 M CsOH aq. and then the polymer was thoroughly washed with distilled water. EPMA spectrum shows existence of Cs atom in the polymer, that is, this plasma polymer after the LiI treatment behaves as an ion-exchanger. The S/Cs ratio indicates that the 90-95% of sulfur atom in the polymer contribute to ion-exchange. The result agreed with analytical data of ESCA shown in Fig.1.

A depth profile of Cs distribution shown in Fig.3 indicates that Cs does not accumulate on the surface, that is, distribution of sulfonic acid group is also uniform throughout the cross-section. The cross-sectional SEM figure shows that the plasma polymer film was about 1.3 μm and pinhole-free in scale of SEM observation.

Figure 4 shows the temperature dependences of the ionic conductivity of the hybrid polymer electrolyte [plasma polymers which contain Li^+ (0.3 or 0.1wt%) - PEO (10wt%)]. An electrical resistance of the hybrid films (1 μm thick) per unit area was also in Fig.4 at right ordinate. The change in slope of conductivity vs. T^{-1} was observed at about 30 °C. The similar temperature dependence was reported on the conventional polymer-alkali metal salt system.12) This dependence fitted with

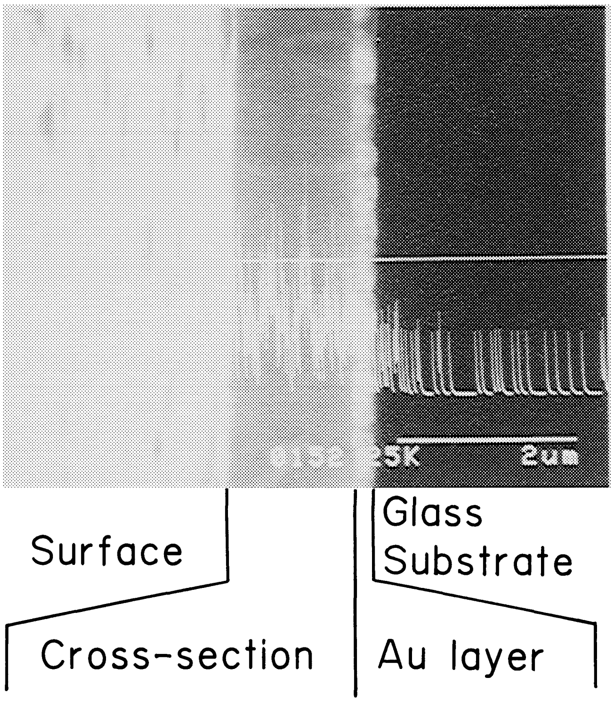

Fig. 3. Depth profile of Cs distribution of plasma polymer.

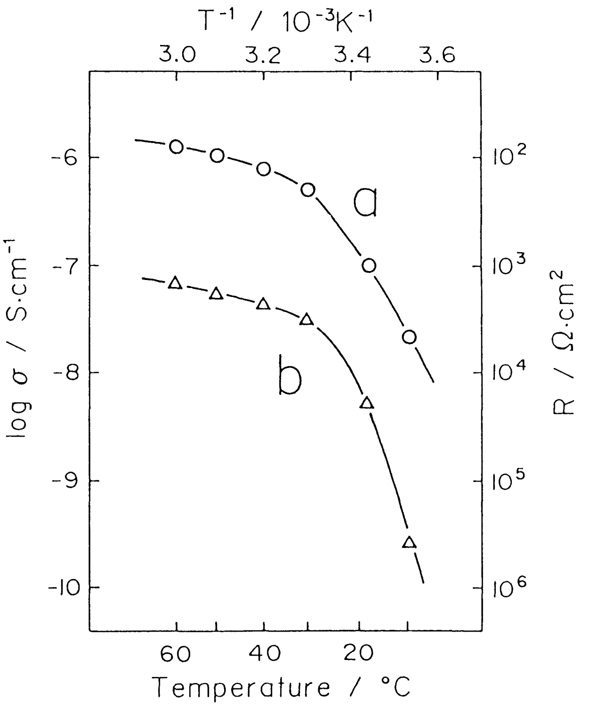

Fig. 4. Temperature dependence of ionic conductivity for hybrid polymer containing Li^+ (a:0.3wt%, b:0.1wt%) and PEO (10wt%).

the WLF type equation[13,14] rather than the Arrhenius type equation.[12] The present polymer also fitted with the WLF type equation.

Because the polarity of siloxane part in this polymer must be as low as polysiloxane, PEO segment should mainly contribute to the ionic dissociation of lithium sulfonate.[15,16] Conductivity of hybrid film [plasma polymer containing Li^+(0.3wt%) - PEO (10%)] reached 1.3×10^{-6} S/cm (80 $\Omega\cdot cm^2$) at 60 °C. Ionic conductivity of this hybrid polymer electrolyte is comparable with those of other solid polymer electrolytes with only one mobile species.[6-8] The hybrid polymer electrolyte is strongly adherent on various substrates, and is pinhole-free and uniformity in film thickness. Therefore it is promising for electrochemical applications, such as all-solid-state lithium batteries, sensors and display devices.

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